



Physical CHEMISTRY

An Indian Journal

Trade Science Inc.

Short Communication

PCAIJ, 7(2), 2012 [74-76]

Superposition model analysis for the zero-field splitting of Mn^{2+} in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$

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PACS No: 76.30F

Received: 29th November, 2011 ; Accepted: 6th January, 2012

ABSTRACT

The Newman superposition model has been applied to second-order zero-field splitting parameter b_2^0 for Mn^{2+} in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$. It is shown that calculated value of b_2^0 is in agreement with the experimental value if local lattice relaxations are taken into account.

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KEYWORDS

Superposition model;
Electron paramagnetic resonance;
 Mn^{2+} ;
Zero-field splitting.

INTRODUCTION

Since the electron paramagnetic resonance (EPR) of S -state ions is easily detectable even at room temperature, many EPR investigations resulting in the determination of zero-field splitting (ZFS) parameters in single crystals have been reported in the literature. In most of these systems the S -state ions were coordinated by oxygen and the ZFS parameter b_2^0 is quite sensitive with respect to small structure changes. The calculations of ZFS follow two approaches. In the first, which is referred to as *ab-initio* calculation, the ZFS is generally calculated using an electrostatic model of the crystal field, together with one or more of the splitting mechanisms. The second method of estimating the ZFS is by the Newman empirical superposition model (SPM) relating the fine structure constants to the actual arrangements of ligands around the impurity^[1]. The SPM has proved to be a very powerful tool in probing the local structure of S -state ions in a variety of compounds^[2]. In

particular, the method has been successfully applied to gain very detailed information on the lattice site and crystalline environment of Mn^{2+} in a number of systems. This paper describes the SPM analysis of the trigonal spectra of Mn^{2+} in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$ (NMN) at room temperature. The EPR data have been taken from the literature^[3] and the analysis is restricted to the largest ZFS parameter b_2^0 .

SUPERPOSITION MODEL

The SPM is based on two assumptions: (i) the total ZFS experienced at an ion in a crystal is due to the close neighbour ions only and (ii) the ZFS at one ion caused by the second ion is intrinsic to that ion pair, i.e. is dependent upon exactly what ions are present and the distance between them, irrespective of the other surrounding. In the SPM, the total ZFS at the central ion is therefore given by a sum of axially symmetric contributions of the ligands i of MX_i unit only. The contri-

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butions of more distant neighbours as well as the interactions between the ligands are ignored^[4]. Two sources of ZFS may be distinguished (i) contribution of the overlap and covalency and (ii) contribution of the crystal field. The former mechanism was shown to be superimposable as long as charge transfer and overlap remain small^[4]. The analysis of the superimposability of the crystal field contribution to ZFS is very complicated. The SPM must hold for crystal field itself and second the spin-Hamiltonian parameter must be linear in crystal field. The analysis of Gd³⁺ ion ZFS indicated that contribution to b_2^m nonlinear in the crystal field is indeed small and the same hold for Mn²⁺ ion^[5]. The above conclusion justifies the assumptions of SPM quite satisfactorily. However, it is very unlikely that SPM postulates hold precisely. There may be significant contribution from ions more distant than the neighbouring ligands. Zhou^[6], has shown, using point charge model, that in BaZnF₄:Mn²⁺, contribution to ZFS from next nearest Zn²⁺ and Ba²⁺ ions are too small to be taken into consideration. The main limitation in applying SPM is to determine exactly the position of the ligands^[1,4] EPR study is usually done on the paramagnetic ion diluted with diamagnetic host lattice. One has to use the positional parameters of the pure host lattice, but the true bond distances and distortions for the impurity ion may differ appreciably. However, the relaxation effects are likely to be smallest for pairs of host and impurity ion having the same valency and similar ionic radii.

The ZFS parameter b_2^0 is written as

$$b_2^0 = \sum K_2^0(\theta_i, \varphi_i) b_2(R_i) \quad (1)$$

where $K_2^0 = (1/2)(3 \cos^2 \theta - 1)$ is the coordination factor, the summation runs over all ligands, R_i , θ_i , φ_i are the spherical coordinates of the i -th ligand (paramagnetic ion is placed at the origin). $b_2(R_i)$ is a scalar quantity, called the second-order intrinsic ZFS parameter. It depends on the ionicity of ligands and is generally agreed to be approximately constant for different compounds with the same metal-ligand combination^[4]. In the SPM framework it is assumed^[1], that the change of $b_2(R_i)$ on going from a reference distance R_0 to another R_1 is given by the empirical power law^[4].

$$b_2(R_i) = b_2(R_0) (R_0/R_i)^{t_2}$$

where the power law exponent t_2 is 7 ± 1 for Mn²⁺. $R_0 = 0.22$ nm is the reference distance for Mn²⁺ sur-

rounded by six oxygens^[4]. The value of $b_2(R_0) = -0.05$ cm⁻¹ is used^[4]. This value is obtained experimentally from the analysis of the spin-Hamiltonian parameter b_2^0 corresponding to Mn²⁺ placed in different lattices, all of which have same ligands (oxygen or water) and the same coordination number 6^[4].

RESULTS AND DISCUSSION

The crystal structure of Ce₂Mg₃(NO₃)₁₂·24H₂O (CMN) isomorphous to NMN has been studied by Zalkin *et al*^[7]. The primitive cell of NMN containing one formula unit is rhombohedral. The space group is $R\bar{3}$. The lattice parameters in hexagonal setting are $a = 1.1$ nm, $c = 3.459$ nm^[7]. The unit cell parameters for CMN are $a = 1.1004$ nm, $c = 3.4592$ nm. The rhombohedral unit cell contains three divalent ions situated at two different lattice sites. One occupies the C_{3i} point symmetry site (site I) and the other two occupy the C₃ point symmetry site (site II). The divalent ions are surrounded by six water molecules forming a nearly octahedral complex. Each Nd³⁺ is coordinated with twelve oxygen ions belonging to six nitrate ions, located at the corners of a somewhat irregular icosahedron.

The EPR of Mn²⁺ in NMN shows the presence of two inequivalent Mn²⁺ centres of unequal intensity. The Mn²⁺ substitutes for Mg²⁺ and shows the spectrum of two Mn²⁺ complexes. It was found that the principal z axes of two [Mn(H₂O)₆]²⁺ complexes are along the c axis and x axis is perpendicular to the c axis. The zero-field splitting parameter $b_2^0(D)$ of Mn²⁺ at site I is and II are -187.2×10^{-4} cm⁻¹ and 19.4×10^{-4} cm⁻¹, respectively^[3]. Mg²⁺ in NMN at site I is surrounded by six water molecules at a distance of 0.2058 nm. The detailed crystal structure of NMN has not been determined. However, it is expected that bond lengths of Mg²⁺-H₂O in NMN would not be very different from that of Mg²⁺-H₂O in CMN. In the SPM analysis the structural data of CMN is used. Mg²⁺ in NMN at site I is surrounded by six water molecules at a distance $R = 0.2058$ nm and at site II is surrounded by two sets of three water molecules each as nearest neighbours at distances 0.2056 nm and 0.2058 nm^[7]. The angle θ that Mg-O makes with the c axis at site I is 54.10° and for site II are 54.83° and 123.69° . The calculated value

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of ZFS parameter D is $-75.7 \times 10^{-4} \text{ cm}^{-1}$ and $104.8 \times 10^{-4} \text{ cm}^{-1}$. The SPM predicts the correct sign. The calculated value of D for site I is smaller than the experimental value and larger for site II.

In these calculations, the assumption has been made that the crystalline structure in the vicinity of the magnetic ion is unchanged from those of the host lattice. The difference in calculated and experimental values of D may be, in principle, due to local relaxation. It has been shown that if R (metal-ligand bond distance) $>$ normal Mn-ligand bond distance, the introduction of substitutional Mn^{2+} gives rise to an inward relaxation while the opposite occurs for $R <$ Mn-ligand bond distance^[9]. The ionic radii of Mg^{2+} and Mn^{2+} are 0.066 nm and 0.080 nm^[8]. Therefore, Mn^{2+} substitution for Mg^{2+} would allow some expansion of O^{2-} octahedron around manganese. A movement of oxygen along the c axis is assumed such that Mn-oxygen bond length increases from that Mg-oxygen. This causes a change in the value of θ . It is found that an increase of about 1.454% in bond lengths (from 0.2058 to 0.2088 nm) causes the angle θ to change to 53° for site I. An increase of about 0.9% in bond length for site II causes θ to change to 54.33° and 124.33° . These values of R and θ leads to b_2^0 values $-187 \times 10^{-4} \text{ cm}^{-1}$ and $19.5 \times 10^{-4} \text{ cm}^{-1}$ for site I and II respectively. A change of bond lengths of about 3%-4% is observed from EXAFS measurements in KZnF_3 and KCdF_3 doped with Mn^{2+} ^[9].

In conclusion, with the use of the SPM, it is possible to obtain the ZFS parameter b_2^0 for Mn^{2+} in host lattice studied from crystal structure data by taking into account the local relaxation effects.

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